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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : C08L 33/12, B32B 27/30, B29D 7/00		A1	(11) International Publication Number: WO 00/08098 (43) International Publication Date: 17 February 2000 (17.02.00)
(21) International Application Number: PCT/GB99/02329		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 4 August 1999 (04.08.99)			
(30) Priority Data: 9817048.3 5 August 1998 (05.08.98) GB 60/097,072 19 August 1998 (19.08.98) US 60/099,055 3 September 1998 (03.09.98) US			
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(54) Title: ACRYLIC MATERIAL			
(57) Abstract			
<p>An acrylic capstock material comprising 40 – 100 % by weight of an acrylic copolymer made by polymerising a monomer mixture comprising 50 – 99 % by weight of methyl methacrylate (MMA) and 1 – 50 % by weight of an alkyl acrylate; and 0 – 60 % by weight of an impact modifier in the form of discrete particles each having a multi-layer structure, wherein said capstock material has a melt flow index of at least 1.5, measured as described in ASTM D-1238 using a 3.8 kg load at 230 °C. The capstock is suitable for extrusion at temperatures below 200 °C e.g. for coextrusion onto PVC polymers.</p>			

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Acrylic material

The present invention relates to acrylic capstock formulations.

Acrylic materials are known for use in capstock applications, for example to provide a tough coating layer over a substrate thermoplastic material. In this way the

- 5 characteristics of the capstock material may be imparted to an article which is made from a substrate which has different characteristics. Acrylic materials are a good choice as a capstock because of their properties of toughness, stability, weatherability and appearance.

Acrylic capstock materials and a method of extruding a composite which includes a
10 capstock are described in US-A- 5,318,737. The patent describes the use as a capstock of a high molecular weight acrylic resin which has a relatively high melt viscosity (melt flow index (MFI) from about 0.4 to about 0.75) for coextrusion onto acrylonitrile-butadiene-styrene (ABS) plastics in particular. The high molecular weight acrylic layer provides a laminate which is suitable for further forming into bathtubs and
15 other items of sanitaryware.

Acrylic materials have particularly good resistance to weathering and therefore acrylic capstock materials are particularly useful to provide a weather resistant outer layer over building components such as cladding, window frames, doors etc, which are often fabricated from structural thermoplastic materials such as polyvinyl chloride (PVC) or
20 ABS. US-A-4189520 describes an extrusion process for providing an acrylic covering layer on a PVC structural member, in particular for window profile extrusions. The PMMA used is of relatively high molecular weight (about 120,000 - 180,000 daltons).

- Composite materials which include a capstock layer over a substrate thermoplastic layer are normally formed by coextrusion of the layers together to form the composite. In the
25 coextrusion of two or more thermoplastic materials, it is normally necessary to match the viscosities of the materials in order to achieve a satisfactory result. When the materials to be coextruded have different viscosities at the desired temperature for extrusion, coextrusion may be difficult, requiring special die designs to provide large flow paths, or incorporating heaters. The problem of matching the viscosities of coextruded plastics is
30 discussed in US-A-5318737, particularly in regard to certain substrates such as PVC

which are thermally degradable at the normal extrusion temperatures of an acrylic capstock material. The use of multi-manifold dies may overcome this problem by enabling different extrusion conditions to be used for each material. Although the use of such technology may enable certain capstock materials to be used, the production of an even, thin coating may still cause problems so thick layers of capstock are often applied to ensure complete coverage of the substrate by the capstock material.

The coextrusion of acrylic capstocks onto PVC materials provides particular problems because PVC is normally extruded at temperatures in the range 190 - 210 °C. Foamed PVC has to be extruded at even lower temperatures, between 160 - 190 °C to control the foaming process and thus the subsequent performance of the extruded article. Acrylic materials are normally extruded at temperatures above 220 °C, at which temperatures PVC starts to degrade. Therefore the coextrusion of acrylic materials onto PVC may lead to thermal degradation of the underlying PVC, resulting in an article which may have degraded physical properties. The temperature at which an acrylic material is processed has a marked effect on its viscosity and rheological properties so that at lower temperatures it is of relatively high viscosity and therefore unsuitable for extruding as a thin layer because of its decreased ability to flow onto the substrate. It is desirable to be able to form a thin layer of the capstock because it is usually relatively expensive compared to the substrate.

- 20 One requirement for an acrylic capstock for use on building components such as cladding or window profiles is that it is tough and resistant to impact. It is known to improve the toughness of such materials whilst maintaining acceptable weathering properties by adding impact modifiers such as core-shell acrylic particles for example. Whilst these modifiers have a beneficial effect on toughness, acrylic compositions which include impact modifiers tend to have higher melt viscosities. US-A-5700566 describes composites of acrylic capstocks containing impact modifying particles and ABS substrates to use to form bathtubs. The acrylic capstock materials described in US-A-5318737 also contain impact modifier particles but are low viscosity materials which are particularly suitable for coextrusion with ABS.
- 30 It is therefore an object of the invention to provide an acrylic capstock formulation which is suitable for coextrusion onto PVC, including foamed PVC, and which overcomes some of the above problems.

According to the invention, an acrylic capstock material comprises 40 - 100% by weight of an acrylic copolymer made by polymerising a monomer mixture comprising 50 - 99% by weight of methyl methacrylate (MMA) and 1 - 50% by weight of an alkyl acrylate; 0 - 60% by weight of an impact modifier in the form of discrete particles each having a multi-layer structure, and optionally additives selected from lubricants, colourants, stabilisers, gloss modifiers, wherein said capstock material has a melt flow index of at least 1.5, measured as described in ASTM D-1238 using a 3.8 kg load at 230 °C.

According to a second aspect of the invention we provide a composite article comprising a structural layer of a thermoplastic polymer and a covering layer comprising an acrylic capstock material which comprises 40 - 100% by weight of an acrylic copolymer made by polymerising a monomer mixture comprising 50 - 99% by weight of methyl methacrylate (MMA) and 1 - 50% by weight of an alkyl acrylate; and 0 - 60% by weight of an impact modifier in the form of discrete particles each having a multi-layer structure, and optionally additives selected from lubricants, colourants, stabilisers, gloss modifiers, wherein said capstock material has a melt flow index of at least 1.5, measured as described in ASTM D-1238 using a 3.8 kg load at 230 °C.

According to a third aspect of the invention, we provide a process for making a composite article comprising a structural layer of a thermoplastic polymer and a covering layer comprising an acrylic capstock material which comprises 40 - 100% by weight of an acrylic copolymer made by polymerising a monomer mixture comprising 50 - 99% by weight of methyl methacrylate (MMA) and 1 - 50% by weight of an alkyl acrylate; and 0 - 60% by weight of an impact modifier in the form of discrete particles each having a multi-layer structure, and optionally additives selected from lubricants, colourants, stabilisers, gloss modifiers, wherein said capstock material has a melt flow index of at least 1.5, measured as described in ASTM D-1238 using a 3.8 kg load at 230 °C; by coextruding through a coextrusion die a first stream of material from a first extruder barrel comprising the structural thermoplastic polymer layer and a second stream of material comprising the acrylic capstock material from a second extruder barrel and cooling the coextruded composite article following its exit from the die.

The alkyl acrylate is selected from the lower alkyl acrylates known for use in acrylic materials which are C₁ - C₁₀, preferably C₁ - C₄ alkyl acrylates. Preferred acrylates include

butyl- (BA), ethyl- (EA) and methyl- (MA) acrylates. More than one acrylate may be present in the composition. The amount of acrylate material in the copolymer may vary according to the nature of the acrylate material. For example, when the composition is made from a MMA/BA copolymer the amount of BA is preferably in the range 5 - 25% by weight. When the acrylate used is ethyl acrylate, about 5 - 35% of acrylate is preferably used. When the acrylate used is methyl acrylate, about 5 - 40% of acrylate is preferably used.

The acrylic copolymer preferably has a molecular weight (Mw) of less than 180,000, more preferably < 140,000 and especially preferably < 120,000, and the Mn is most preferably in the range 80,000 - 100,000. The Mn is preferably in the range 30,000 - 50,000 and the polydispersivity is normally in the range 2 - 2.4. The polymer may additionally contain residues of a chain transfer agent or initiator or other processing additive such as stabilisers etc.

The composition contains 0 - 60% by weight of an impact modifier which is in the form of discrete particles each having a multi-layer structure, known in the art as "core-shell" particles. Preferably the composition contains at least 10 %wt of impact modifier, e.g. 25 - 50%. Typical core-shell particles are formed by emulsion polymerisation and comprise a PMMA core, a rubbery first shell of a styrenic copolymer with an alkyl acrylate and an outer shell of methyl methacrylate or a copolymer thereof and numerous examples have been described in the art. A preferred core-shell particle comprises a (meth)acrylic polymer core, a first shell comprising a low Tg polymer comprising 0 - 25% by weight of a styrenic monomer and 75 - 100% of a (meth)acrylic monomer, the (meth)acrylic monomer being capable of forming a homopolymer having a Tg in the range -75 to -5 °C, the first shell representing at least 65% by volume of the combined volume of the core and first shell, and optionally a second shell which comprises a second (meth)acrylic polymer which may be the same as or different from the first (meth)acrylic polymer and the core and first shell together contain from 0.5 - 1.0 % by weight of a graft cross-linker. Suitable particles are described in WO96/37531.

The composition has a melt flow index (MFI), measured by ASTM D-1238 using a 3.8 kg load at 230 °C, of at least 1.5. Preferably the MFI is in the range 2.0 - 35, more preferably 3 - 20, e.g. 3 - 15. A particular feature of the composition is that it has the required melt viscosity to enable it to be coextruded onto a plastic substrate at temperatures below 200

°C, and so it is suitable for coextrusion onto PVC or foamed PVC. Foamed PVC is particularly sensitive to high temperatures and thus is normally not exposed to fabrication temperatures above about 160 - 190 °C. Therefore the composition of the invention is especially suitable for coextrusion onto foamed PVC articles. However, the composition 5 may be extruded onto other substrates, e.g. ABS thermoplastics, and at normal acrylic processing temperatures if required. For example, the composition may be coextruded onto an ABS substrate at temperatures in the range 190 - 260 °C.

The composition may optionally contain additives such as pigments, dyes, gloss-modifying compounds, UV stabilisers, thermal stabilisers, lubricants etc.

- 10 The acrylic capstock material may be applied as a relatively thin layer, i.e. at a thickness of less than about 500 µm. In many applications it is preferred to apply the capstock material at a thickness in the range 50 - 250 µm, especially 100 - 200 µm. The capstock composition of the present invention is especially suitable for forming such thin layers by extrusion.
- 15 The structural thermoplastic may be any of those normally used in the art e.g. ABS, but in a preferred form the structural thermoplastic comprises polyvinyl chloride (PVC), including foamed PVC. The PVC may contain stabilisers, pigment, and other additives commonly found in extruded PVC polymers as known in the art. The structural thermoplastic layer may be planar to form a composite sheet material, or may be formed into a more complex shape which may be hollow, e.g. in some forms of window profile; or solid, e.g. for 20 building profile such as that used for cladding.

The acrylic compositions are suitable for extrusion directly onto a plastic substrate, for example by coextrusion in which the acrylic composition is extruded over an extrusion of the substrate to form a covering layer of acrylic on the substrate. The acrylic may be 25 extruded on a range of extrusion equipment, i.e. using single-screw or twin-screw extruders and dual manifold dies in addition to feedblock coextrusion systems. Although coextrusion is the preferred method for forming a layer of the acrylic material over the substrate, it is possible to form the acrylic layer separately and then secure it to the substrate. The acrylic capstock material may be applied to more than one face or surface 30 of the structural thermoplastic, e.g. to form a three layer composite sheet or to form a profile having an acrylic covering layer over some or all of its exposed surfaces.

The invention will be further described in the following examples.

Examples 1 - 6 Preparation of acrylic composition

The acrylic polymer was prepared by suspension polymerisation of 85 % by weight of methyl methacrylate and 15% by weight of butyl acrylate with 0.375% of lubricant and 5 0.34% of chain transfer agent and 0.23% of AIBN initiator. The molecular weight of the polymer was about 80 - 100,000 (measured by gel permeation chromatography against PMMA standards) and the MFI 35 - 40 g/10mins (ASTM D-1238 3.8 kg at 230 °C). Acrylic compositions (one unpigmented, the rest coloured) were prepared by melt-blending the constituents in a twin-screw extruder at a temperature in the range 230 - 250 °C. The 10 formulations and measured MFI data is given in Table 1.

Table 1

Formulation (wt%)	1	2	3	4	5	6	7	8
Acrylic polymer	49.71	81.70	71.73	61.77	47.32	42.34	45.87	91.65
impact modifier	44.50	10.00	20.00	30.00	44.50	44.50	40.98	-
gloss modifier	5.00	-	-	-	-	5.00	5.06	-
colour masterbatch	-	7.40	7.40	7.40	7.40	7.40	7.37	7.40
UV stabiliser	0.50	0.50	0.50	0.50	0.50	0.50	0.46	0.50
thermal stabiliser	0.10	-0.10	0.10	0.10	0.10	0.10	0.09	0.10
lubricant	0.19	0.30	0.27	0.23	0.18	0.16	0.17	0.35
MFI (230 °C, 3.8 kgs) g/10mins	3.40	24.30	15.40	9.80	4.50	3.70	3.70	32.40

Extrusion onto PVC substrate

A coextrusion process was set up and operated having a main extruder consisting of a conical twin-screw extruder and operating at approximately 13.5 rpm in which the barrel 15 temperature increased from 110 °C at the feed end to 185 °C at the die end. A second extruder (single-screw) was provided to extrude the capstock. A solid PVC was extruded through the main extruder. A dual manifold die produced a rigid PVC box window profile from the main extruder with an acrylic capstock layer from the second extruder.

The barrel temperature of the second extruder was set up to vary from 180 - 185 °C. The 20 clear acrylic formulation of Formulations 1 & 8 was extruded through the second extruder into the coextrusion die using various screw speeds to produce four different thicknesses

of acrylic layer (100, 150, 200 & 300 µm) on the PVC window profile. The capstock covered the profile completely, with no show-through of the substrate material.

Extrusion of coloured acrylic material

- The coextrusion arrangement was repeated but using one of the coloured acrylic formulations of Formulations 2 - 6 in the second extruder instead of the unpigmented material. Acrylic capped window profile was produced which had four different thicknesses of acrylic layer ranging from about 100 to about 300 µm. It was noted that the coloured material hid the substrate PVC very effectively, with little or no show-through of the PVC material, even when the shape of the profile provided a sharp edge or corner.
- 10 This indicated that the acrylic composition conformed well to the substrate and did not thin out over sharp edges due to the rheological properties of the melt.

Extrusion onto foamed PVC substrate

- A conical twin-screw PVC foam extruder was used to extrude foam cladding at a melt temperature of 163 °C. Acrylic compositions as described in Formulation 1 - 6 was extruded through a secondary extruder as described above to coextrude the acrylic layer onto a PVC foam substrate. The resulting coextrusion was passed through foam sizing equipment. The acrylic layer was extruded at several thicknesses between 100 and 500 µm.

Impact testing

- 20 Samples of acrylic capped foam cladding made as described above and having an average capstock thickness of about 150 µm was tested for impact performance by means of a falling weight impact test as described in British Standard BS 7619. The drop height was increased until the sample failed, e.g. by splitting or cracking observed in the impacted sample. BS 7619 specifies that a material passes the test when no cracks or 25 splits are visible in the profile following a impact from a drop height of 0.31m. All samples tested passed this requirement.

Table 2

Capstock formulation	2	3	4	5	6
Falling weight failure height (m)	1.3	1.5	1.5	1.4	1.4

Aged impact performance

Samples of PVC foam capped with acrylic capstock of Formulation 6 were aged for 1000 hours under QUV A exposure at 50 °C as specified in BS 7619 and tested again with the falling weight. A PVC capped PVC foam sample was made by the method described above but using PVC in the secondary extruder instead of the acrylic composition as a comparative sample. The impact performance of this sample was also tested according to BS 7619. BS 7619 specifies that an aged material passes the test when no cracks or splits are visible in the profile following a impact from a drop height of 0.15m. All samples tested passed this requirement. The results are shown in Table 3.

Table 3

	Aged		Unaged	
	Thickness (µm)	Failure height (m)	Thickness (µm)	Failure height (m)
Comparative (PVC-capped foam)	450	0.90	500	1.5
	300	0.8	350	1.1
	200	0.60	200	0.9
Foam capped with Example 6 acrylic	400	1.0		
	200	0.9		
	100	0.7		
Foam capped with Example 7 acrylic			500	1.4
			250	1.1
			100	0.9

- 10 The mechanical properties of the acrylic capped PVC materials are comparable with the PVC capped material, but have the benefits of weatherability associated with acrylic materials. The use of acrylic compositions according to the invention enables very thin layers of acrylic material to be applied to the substrate by coextrusion, whereas this is very difficult to achieve using conventional acrylic formulations. The compositions of the 15 invention are therefore beneficial for use on large-area or intricately shaped commercial extrusions such as window profiles, door panels, building profiles etc.

Example 7 Extrusion onto ABS substrate

- The capstock composition of Formulation 1 was coextruded through a single-screw extruder at temperatures of 190 - 210 °C onto a Dow 3904 high impact ABS substrate 20 extruded through a main twin-screw extruder at about 190 - 210 °C. By varying the screw speed on the co-extruder, capstock thicknesses of about 225 µm and 130 µm were produced.

Claims

1. An acrylic capstock material comprising 40 - 100% by weight of an acrylic copolymer made by polymerising a monomer mixture comprising 50 - 99% by weight of methyl methacrylate (MMA) and 1 - 50% by weight of an alkyl acrylate; and 0 - 60% by weight of an impact modifier in the form of discrete particles each having a multi-layer structure, wherein said capstock material has a melt flow index of at least 1.5 g/10mins, measured as described in ASTM D-1238 using a 3.8 kg load at 230 °C.
2. An acrylic capstock material as claimed in claim 1, wherein the acrylic copolymer has a molecular weight (Mw) of less than 180,000 daltons.
- 10 3. An acrylic capstock material as claimed in claim 2, wherein the acrylic copolymer has a molecular weight (Mw) in the range 80,000 - 120,000 daltons.
4. An acrylic capstock material as claimed in any of claims 1 -3, comprising at least 20 %wt of impact modifier.
- 15 5. An acrylic capstock material as claimed in any preceding claim wherein when the alkyl acrylate monomer content is selected from butyl acrylate at a level in the range 5 - 25% by weight, ethyl acrylate at a level in the range 5 - 35% or methyl acrylate at a level in the range about 5 - 40%.
6. An acrylic capstock material as claimed in any preceding claim wherein the capstock material has a melt flow index of at least 3.0 g/10mins.
- 20 7. A composite article comprising a structural layer of a thermoplastic polymer and a covering layer comprising an acrylic capstock material which comprises 40 - 100% by weight of an acrylic copolymer made by polymerising a monomer mixture comprising 50 - 99% by weight of methyl methacrylate (MMA) and 1 - 50% by weight of an alkyl acrylate; and 0 - 60% by weight of an impact modifier in the form of discrete particles each having a multi-layer structure, and optionally additives selected from lubricants, colourants, stabilisers, gloss modifiers, wherein said capstock material has a melt flow index of at least 1.5, measured as described in ASTM D-1238 using a 3.8 kg load at 230 °C.

8. A composite article as claimed in claim 7, wherein the structural thermoplastic is selected from PVC and ABS polymers.
9. A composite article as claimed in claim 8, wherein the structural thermoplastic layer is in the form of a sheet, solid or hollow shaped article.
- 5 10. A composite article as claimed in any of claims 7 - 9, wherein the acrylic capstock composition is applied to more than one face of the structural thermoplastic layer.
11. A composite article as claimed in any of claims 7 - 10, which is in the form of a door, window profile, cladding panel or other building component.
12. A process for making a composite article comprising a structural layer of a
10 thermoplastic polymer and a covering layer comprising an acrylic capstock material which comprises 40 - 100% by weight of an acrylic copolymer made by polymerising a monomer mixture comprising 50 - 99% by weight of methyl methacrylate (MMA) and 1 - 50% by weight of an alkyl acrylate; and 0 - 60% by weight of an impact modifier in the form of discrete particles each having a multi-layer structure, and optionally additives selected
15 from lubricants, colourants, stabilisers, gloss modifiers, wherein said capstock material has a melt flow index of at least 1.5, measured as described in ASTM D-1238 using a 3.8 kg load at 230 °C; by coextruding through a coextrusion die a first stream of material from a first extruder barrel comprising the structural thermoplastic polymer layer and a second stream of material comprising the acrylic capstock material from a second extruder barrel
20 and cooling the coextruded composite article following its exit from the die..
13. A process as claimed in claim 12 wherein the capstock has a melt flow index of at least 3.0 g/10 mins.
14. A process as claimed in claim 8 or claim 9, wherein the structural thermoplastic polymer is PVC.
- 25 15. A process as claimed in claim 14 wherein the PVC is a foamed PVC.
16. A process as claimed in claim 15, including the step of passing the PVC foam through a foam sizing stage.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/02329

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C08L33/12 B32B27/30 B29D7/00.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L B32B B29D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

27 October 1999

Date of mailing of the international search report

08/11/1999

Name and mailing address of the ISA

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Information on patent family members

International Application No

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